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OPTICAL AND ESR STUDIES ON AN IR ABSORPTION BAND IN CsI:Na AFTER X-RAY IRRADIATION

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We have studied the nature of the defect giving rise to a near IR absorption band (717 nm) in X irradiated CsI:Na by measuring its linear dichroism, its magnetic circular dichroism and its change due to the resonance microwave. The defect ($g_{||} = 1.96$, $g_{\perp} = 2.23$ with axis near $\langle 100 \rangle$) involves a Na^+ ion and an excess electron.

1. INTRODUCTION

X-ray irradiation at low temperature usually creates in alkali halide crystals stable electron and hole centers at the same time, like F and V_K centers. This is not the case in pure CsI crystals, even below 4.2 K.

When CsI doped with NaI is irradiated at low temperature, two optical absorption bands appear at 408 and 717 nm¹. The former one which is independent of doping impurities is attributed to the V_K center². The latter near infrared absorption whose excitation leads to intrinsic recombination luminescence was supposed to be due to an electron trap such as Na^0 ¹.

ESR may be one of the best tools to study the origin of this absorption band as well as its atomic structure. However, ESR observed so far in CsI:Na with direct detection technique is only that of the V_K center². In order to study the origin of this absorption, optical properties of this band including the magnetic circular dichroism (MCD) have been studied. We found ESR with X-band microwaves (9.1 GHz) by an optical detection technique in which the microwave induced change of MCD has been monitored.

2. EXPERIMENTAL

The optical absorption spectrum and its linear dichroism at 4.2 K together with the

excitation spectrum for the 338 nm intrinsic recombination luminescence³ around the absorption band are shown in Fig. 1. The total area of the IR absorption band is about 5 times as large as that of 408 nm band. The linear dichroism, the relative difference of absorption coefficients $\Delta\sigma = (\sigma_{||} - \sigma_{\perp})/(\sigma_{||} + \sigma_{\perp})$, has been measured after the bleaching with 660 nm and 770 nm light linearly polarized parallel to one of the $\langle 100 \rangle$ crystal axes. There is no dichroism apparently in both cases within 5% of experimental error. The excitation spectrum is very similar to the absorption spectrum. The excitation bleaches with equal rates both IR and V_K absorption bands.

The MCD spectra are shown in Fig. 2 for the case in which the magnetic field is applied parallel to $\langle 100 \rangle$ axis; similar results are obtained when the magnetic field is parallel to $\langle 111 \rangle$. They are derivative type curves of the absorption band and they display the same shape over all the measured temperature and magnetic field region. The dependence of the MCD intensity at 680 nm on the temperature and the magnetic field are shown in Fig. 3. The result indicates that the MCD of this band is determined by the so-called paramagnetic term, that is, spin polarization in the ground state.

When the resonant microwave field H_1 is applied at 1.5 K to the crystal with a static magnetic field, the MCD decreases towards zero, since the microwave bleaches the ground state spin polarization; the MCD decreases up to about 20% of its initial value showing a characteristic saturation with increasing microwave power. Since the MCD is determined

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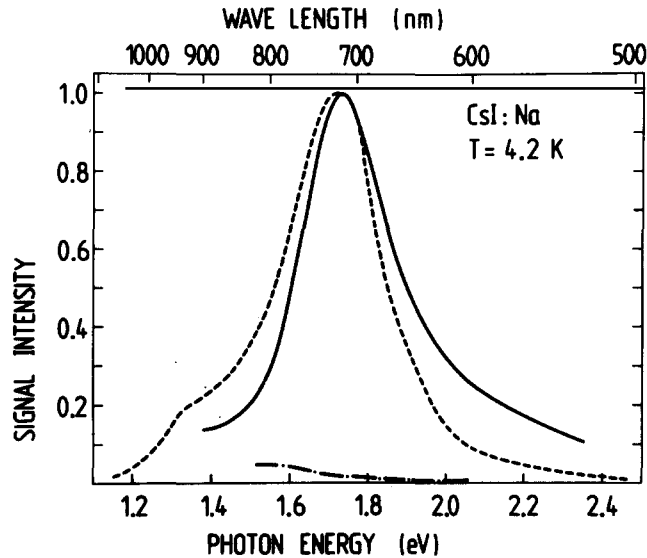


Fig. 1

Solid, dashed and dotted lines show optical absorption (in arbitrary unit), its linear dichroism $(\sigma_{||} - \sigma_{\perp})/(\sigma_{||} + \sigma_{\perp})$, and excitation spectrum (a.u.) of the 338 nm intrinsic recombination luminescence at 4.2 K, respectively, after X-ray irradiation on CsI:Na crystal. Lower and higher energy sides of the absorption measurement are limited by the spectrometer and the glass filter used to cut the luminescence.

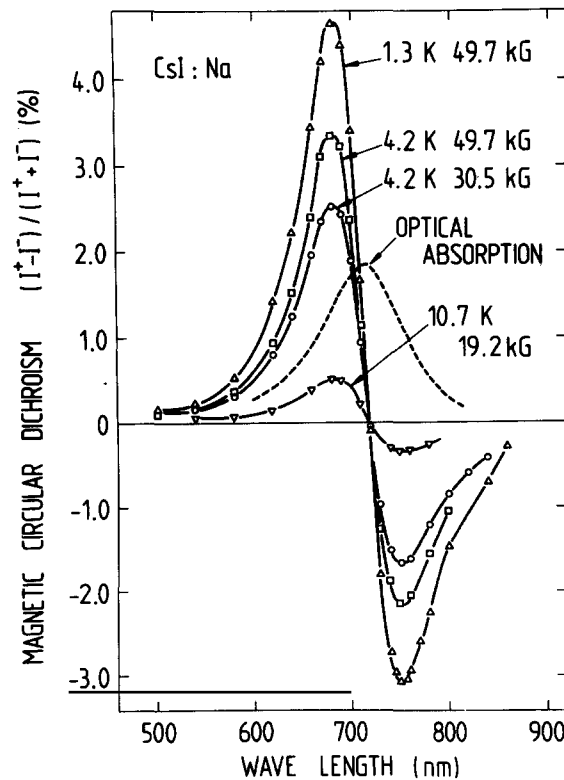


Fig. 2

Magnetic circular dichroism of the IR absorption band on Fig. 1 at several temperatures and magnetic fields.

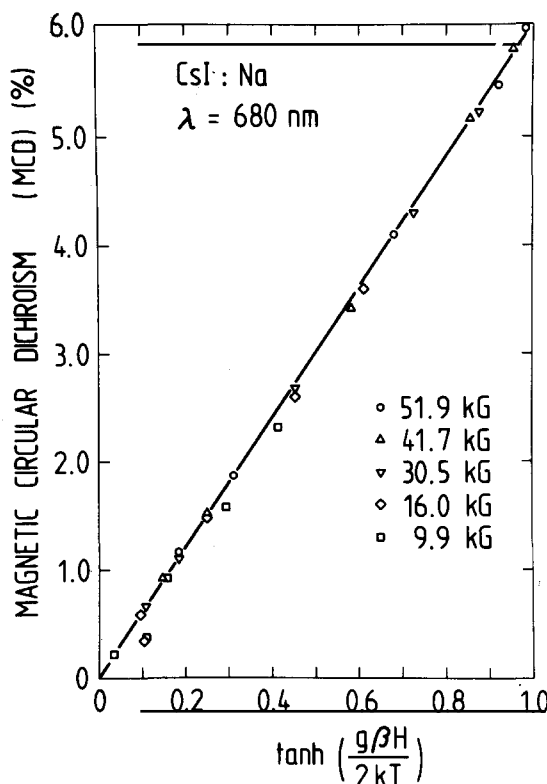


Fig. 3

The dependence of the magnetic circular dichroism intensity at 680 nm on the temperature and on the magnetic field which is applied parallel to $\langle 100 \rangle$.

by spin polarization in these experimental conditions for ESR, one can obtain an ESR spectrum as $[MCD(H_1=0) - MCD(H_1)]/MCD(H_1=0)$ as shown in Fig. 4 (a), (b) when the magnetic field is applied parallel to the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, respectively; the MCD is monitored at 680 nm to give the spectra of Fig. 4.

When the magnetic field is applied parallel to the $\langle 111 \rangle$ direction, the overall features of the ESR spectrum are symmetric around the peak position. When the field is parallel to $\langle 100 \rangle$, the ESR is asymmetric and shows another peak on the higher field side. The similar spectrum has been obtained at 4.2 K. These results, together with the spectrum obtained with the magnetic field parallel to $\langle 110 \rangle$, show that the symmetry of the center is lower than O_h and that its symmetry axis is parallel or near to the $\langle 100 \rangle$ axis.

3. DISCUSSION

ESR spectra have been analyzed by means of the method of moments by assuming the symmetry axis parallel to the $\langle 100 \rangle$ axis and the axial symmetric spin Hamiltonian

$$\mathcal{H} = \beta[g_{||}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + \sum_i \vec{I}_i \cdot \vec{A}_i \cdot \vec{S} \quad (1)$$

where the last term is the hyperfine interaction with nuclei. Furthermore, we tentatively assume isotropic optical absorption coefficient, since there was no linear dichroism. One can obtain $g_{||}$ and g_{\perp} of 1.97 ± 0.02 and 2.23 ± 0.02 , respectively, from the first moments of the ESR spectra under three configurations of the magnetic field. Peak positions according to these g -value are shown in Fig. 4 (a), (b) by solid arrows.

The following facts suggest that the center is associated with an electron; the center is created by X-ray together with the V_k center and the excitation of this IR band enhances the intrinsic recombination luminescence and bleaches the V_k and IR absorption bands. On the other hand, one may imagine a hole center from the rather large positive g -shift of $g_{||}$. One should check the possibility that the IR absorption band is produced by the overlap of two absorption bands due to electron and hole

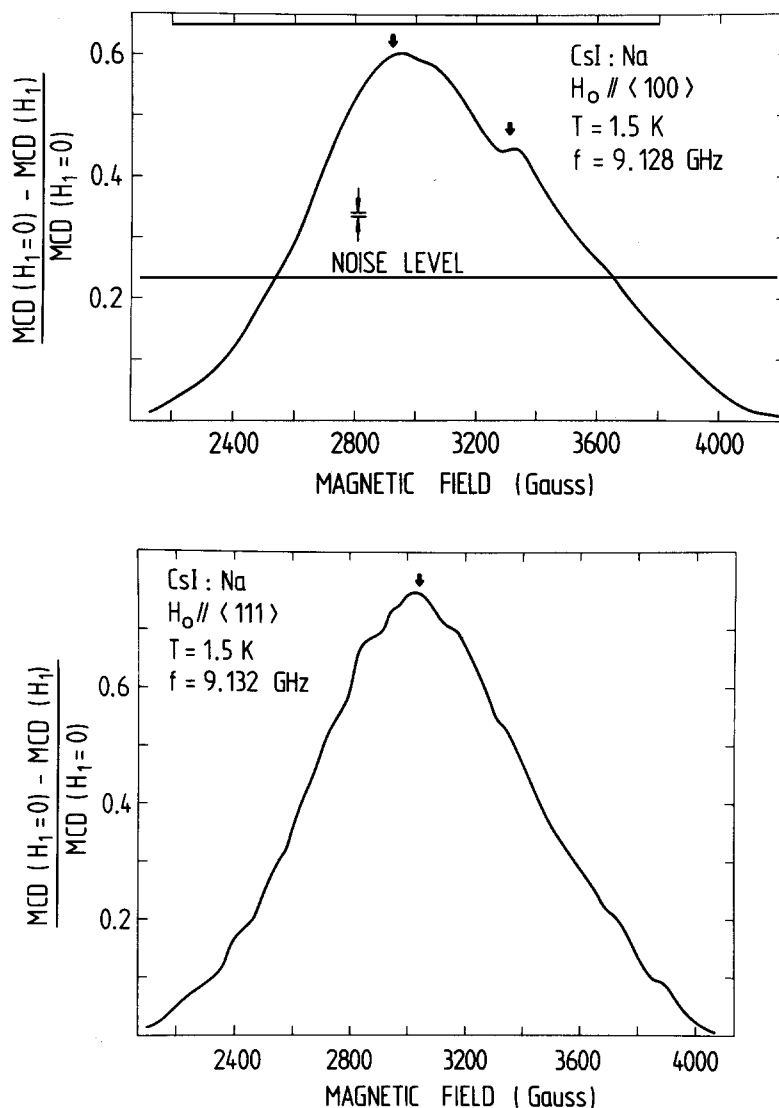


Fig. 4

ESR spectra (a) and (b) obtained by means of the optical detection technique at 1.5 K with the magnetic field parallel to $\langle 100 \rangle$ ($f_0 = 9.128 \text{ GHz}$) and to $\langle 111 \rangle$ (9.132 GHz), respectively.

centers. The following facts suggest that the absorption band, or at least most of it, is due to one center only: (1) the excitation spectrum is very similar to the absorption band; (2) the MCD spectrum is independent of the magnetic field and of the temperature; (3) the ESR spectra obtained by monitoring MCD at 630 and 800 nm are the same as those at 680 nm; (4) the saturation recovery curves of the ESR signal are the same at several magnetic fields over the ESR spectrum.

If the center moves by changing the direction of its symmetry axis, the absence of linear dichroism does not indicate necessarily an isotropic absorption coefficient. It is

possible to fit the first moments within experimental error by using the anisotropic absorption coefficients within the region of $|\Delta\sigma| < 0.4$; the set of g -values is the same as in the previous case. The second moment analysis has been tried with the spin Hamiltonian of eq. (1) and the assumption that the principal axes of the hf tensor are the same as those of the g -tensor. In this analysis, theoretical values can fit the experimental ones only when one introduces the anisotropy of the absorption coefficient. Our assumptions such as isotropy of the absorption coefficient, and the possibility of minor contribution from another center, must be checked by more precise experiments. Furthermore, temperature dependence of ESR

including relaxation time would be interesting to see dynamical effects of this center.

4. CONCLUSION

A paramagnetic center associated with the Na^+ ion and an electron gives the IR absorption band peaked at 717 nm produced by X-ray in $\text{CsI}:\text{Na}$. The center has a symmetry lower than O_h , the principal axis lying around $\langle 100 \rangle$ and

the g -values being $g_{||} = 1.97 \pm 0.02$ and $g_{\perp} = 2.23 \pm 0.02$. This indicates that the paramagnetic spin is not simply due to a 3s electron on a Na^+ ion.

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